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PHOTOLUMINESCENCE OF PbS QUANTUM DOTS ON SEMI-INSULATING GaAs (Postprint)

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Photoluminescence of PbS quantum dots on semi-insulating GaAs

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We studied the emission properties of colloidal PbS quantum dots (QDs) (5.3 nm) dispersed on semi-insulating GaAs in the temperature range of 5–300 K by employing Fourier transform infrared photoluminescence spectroscopy. The results reveal that the PbS QDs alter and notably enhance the emission features of the GaAs substrate itself. The dependence of the QD emission peak position on temperature is modeled equivalently well with the well-known empirical Varshni equation and with a relation based on thermodynamics. The work reveals that emission properties of PbS QDs do not follow predictably general rules but are determined sensitively by the preparation method and substrate used. © 2010 American Institute of Physics. [doi:10.1063/1.3460150]

I. INTRODUCTION

Potential applications in tunable laser sources, light emitting diodes, and display arrays, move the emission properties of nanostructured lead sulfide (PbS) into the center of ongoing research activities.¹ However, before the mastery of the emission of chemistry based PbS quantum dots (QDs) might mature enough to serve in active device structures further basic questions have to be addressed. Stability of the emission is one issue,² while another technologically important matter is the integration of PbS QDs with commonly used semiconductor layers and substrates such as gallium arsenide (GaAs) and related compounds, which are employed in mass-market optoelectronic devices. So far, most of the PL investigations of PbS QDs were performed by using glass hosts or glass carriers.^{1,3–6} In this paper, we address the matter of possible integrated hybrid PbS/GaAs device formation by first investigating photoluminescence (PL) of PbS QDs on commercially available GaAs substrates. Particularly, we focused our activities on the PL temperature dependence and, additionally, we reveal that the presence of PbS QDs alters the emission properties of the GaAs substrate itself.

II. SAMPLE PREPARATION

The PbS QDs, with an average size of 5.3 nm, were purchased from Evident Technologies. The QDs are dissolved in toluene and capped by oleic acid. The QDs were dispersed by a supercritical CO₂ fluid process⁷ on 6 × 6 mm² pieces of a standard semi-insulating (SI) GaAs wafer. Before the QD deposition, the GaAs substrates were thoroughly rinsed with isopropanol and toluene, and afterwards, dried with nitrogen gas.

For the supercritical fluid CO₂ deposition process, a high-pressure stainless steel chamber with a volume of about 16 cm³ was used. The chamber was carefully cleaned with acetone and high-pressure CO₂ liquid or gas. A glass con-

tainer with about 250 μL of the QD solution was set inside the chamber and two pieces of the GaAs substrates were inserted into the solution. One of the GaAs pieces was covered with a transmission electron microscopy (TEM) grid, which was used to estimate the surface coverage and size distribution of the QDs. The chamber was then purged at room temperature with CO₂ gas at 70 atm. The pressure was slowly increased to 100 atm. through a pressure modulator. After closing the inlet valve, the chamber was then slowly heated to 38 °C, while the inside pressure was increased to about 150 atm. The chamber was kept at this condition for about 5 h to allow the QDs to dissolve into supercritical CO₂+toluene liquid phase, and afterwards, the chamber was vented. The QDs deposited on both the GaAs substrate and the TEM grid surfaces were imaged by a scanning electron microscope (SEM). A typical result is shown in Fig. 1. The arrangements of the QDs are rather random but no multiple layers or three-dimensional aggregates are observed over the

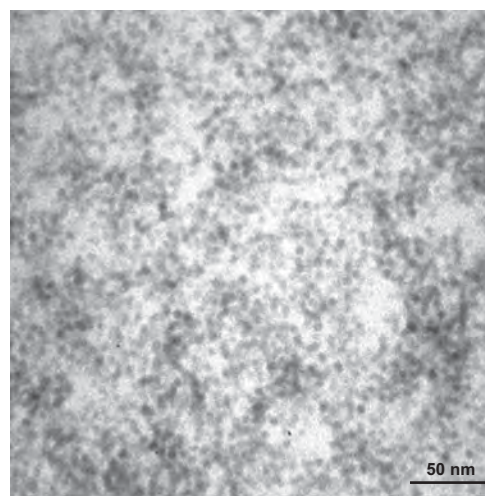


FIG. 1. SEM image of the QDs. The bar on the right hand side corresponds to 50 nm.

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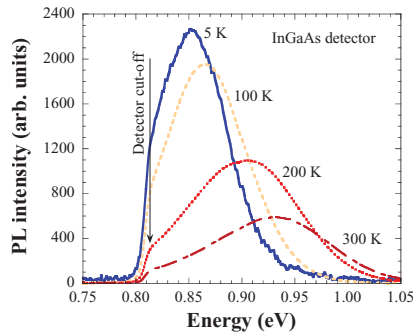


FIG. 2. (Color online) PL spectra of the PbS/GaAs sample at various selected temperatures measured with the InGaAs detector.

entire surfaces. It is evident that the QDs films deposited by this method from a supercritical fluidic environment are much smoother and more uniform than those deposited from solvent evaporation.

III. EXPERIMENT

The PL measurements were carried out by exciting the sample with the continuous wave 532 nm emission of a solid-state laser. The sample was mounted in an optical, liquid helium cooled cryostat equipped with a heater, allowing measurements from 5 to 300 K. A Fourier transform infrared (FTIR) Bomem spectrometer was used to measure the emission spectra. The expected emission of the QDs is around 0.9 eV (1378 nm) at room temperature. Around this spectral range the InGaAs detector would be the optimum choice for data collection. However, at low temperatures the QD PL peak emission shifts to lower energy and starts to move out of range of the InGaAs detector which has a cut-off wavelength of about 1550 nm (0.80 eV). Figure 2 illustrates the situation, showing that PL signals measured with the InGaAs detector exhibit a cut-off around 0.80 eV. Therefore, in order to provide full coverage of the PL peak of the QDs, an InSb detector was employed as well, resulting in two independent PL data sets from two different sample spots. Consequently, slight differences between measurements are not attributed to detector features but to the fact that the data are not collected from exactly the same spot. Additionally, the signal-to-noise ratio is larger for the measurements with the InGaAs detector so the impinging laser intensity on the sample surface was increased from approximately 14 and 80 W/cm² for the measurements carried out with the InGaAs and the InSb detector, respectively. This increase in laser intensity will shift the PL peak position (<3 meV) and alter the temperature dependence slightly.⁸

IV. RESULTS

Figure 3 shows the emission spectra at various temperatures measured with the InSb detector. The peak emission takes place in the range 0.86–0.95 eV, by varying the temperatures from 5 to 300 K. The shift of about 0.5 eV from the bulk PbS band gap value at around 0.40 eV (at 300 K) indicates the highly effective quantum confinement of the PbS nanocrystals. Additionally, the spectra show a broad emis-

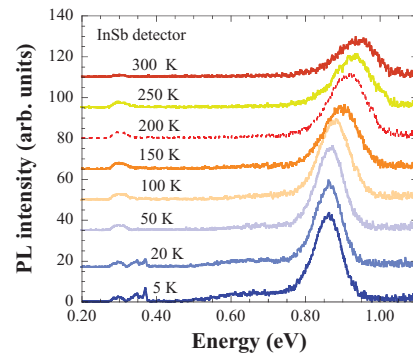


FIG. 3. (Color online) PL spectra of the PbS/SI GaAs sample at various temperatures measured with the InSb detector.

sion peak centered around 0.65 eV. It originates from the well known EL2 defect found in SI GaAs.^{9,10} PL spectra of EL2 related emission are routinely reported at 0.65 and 0.68 eV. What is not reported is the PL spectrum for SI GaAs at lower energies. So, the observed set of 3 peaks below 0.4 eV is a new feature. Defect levels in SI GaAs below 0.4 eV have been reported by other techniques. For example, Fang *et al.*¹⁰ and Martin *et al.*¹¹ reported levels in this range employing normalized thermally stimulated current analysis and Hall measurements, respectively.

The detailed features from 0.25 to 0.4 eV in Fig. 3 are GaAs related. This was checked by examining the shift in these peaks with temperature. These peaks shift to lower energy as the temperature is increased and follows the known temperature dependence of the GaAs band gap. Lead sulfide has the opposite temperature trend, i.e., the band gap increases with increasing temperature. The sharp peak at 0.37 meV has a very narrow full width at half maximum (FWHM) of 5 meV at 5 K. Figure 4 shows the comparison of the PL spectra at 5 K from the bare SI GaAs substrate and the sample with the deposited PbS QDs (PbS/GaAs) for energies below 1.1 eV. Notably, the PbS QDs enhance considerably the substrate PL intensities (a factor of about 5 and more), and enhances the intrinsic emission below 0.4 eV revealing the additional peaks.

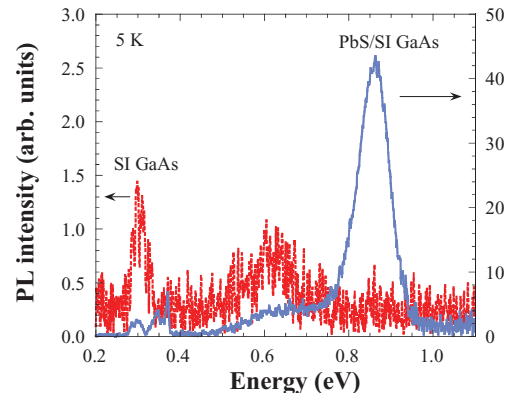


FIG. 4. (Color online) Comparison of the 5 K PL in the midinfrared range of the SI GaAs substrate and the PbS/SI GaAs sample. The spectra are shown in the same arbitrary units.

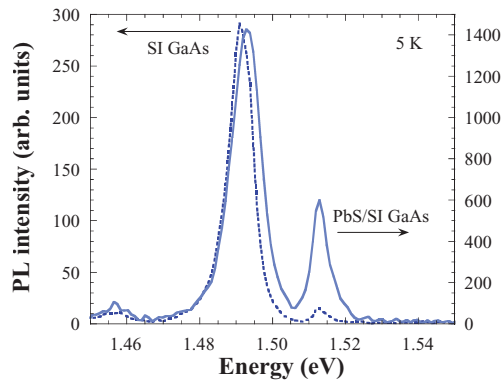


FIG. 5. (Color online) Comparison of the 5 K PL in the near infrared range of the SI GaAs substrate and the PbS/GaAs sample. The spectra are shown in the same arbitrary units.

Similarly, when looking at the GaAs PL spectra near the band gap, utilizing the InGaAs detector, there are additional spectral changes when the PbS QDs are on the GaAs surface. Figure 5 shows the detailed comparison of the PL spectra at 5 K from the bare substrate and the PbS/GaAs sample measured with the InGaAs detector. In this case, the appearance of the band gap emission is not altered but the strong center peak due to donor–acceptor transition¹⁰ appears to be shifted by 2 meV (from 1.4908 to 1.4928 eV) toward higher energies. However, we interpret the PL shift not in terms of band gap energy alteration but due to a FWHM broadening of the PL peak caused by a carrier temperature increase in the SI GaAs substrate covered with PbS QDs with respect to the

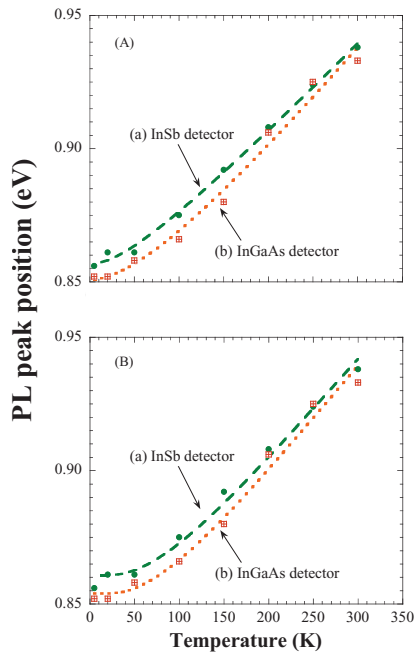


FIG. 6. (Color online) (a) PL peak position vs temperature measured (a) with the InSb detector and (b) with the InGaAs detector. The broken and dotted lines are fitted with Eq. (1). (b) PL peak position vs temperature measured (a) with the InSb detector and (b) with the InGaAs detector. The broken and dotted lines are fitted with Eq. (2).

TABLE I. Fitting parameters used with the Varshni relation.

Detector	$E_g(0 \text{ K})$ (eV)	α (eV/K)	β
InSb	0.8566	0.000 345	75.189
InGaAs	0.8509	0.000 410	124.93

intrinsic bulk material. We further note that the transition at 1.5125 eV, which is due to a free exciton decay,¹⁰ does not reveal a notable FWHM change. However, the intensity of this transition is enhanced. According to the Roosbroeck–Shockley equation,¹² the increase in the FWHM of the donor–acceptor transition and in the overall emitted intensity point to the fact that the carrier temperature in the GaAs substrate covered with PbS QDs is enlarged with respect to the bare GaAs substrate. The growth of the carrier temperature is caused by enhanced Coulomb interaction among the carriers due to carrier transfer from the QDs to the GaAs substrate. The subject of this transfer and in particular the PL enhancement is currently under investigation and requires additional characterizations with surface sensitive methods such as x-ray photoelectron spectroscopy. The results of our ongoing studies will be reported in a forthcoming paper.

In addition to exploring the effects of the PbS QDs on the GaAs PL, we performed systematic temperature dependence studies of the QD PL peak. Figure 6, panels A and B, show the energy position of the PbS QD emission maxima as a function of temperature as measured with both detectors. The overall temperature coefficient of the peak shift is about 0.3 meV/K, similar to the one of PbS QDs on glass above 150 K.⁴ The shift in the QD PL peak in Fig. 6(a) was fitted with the Varshni relation¹³

$$E_g(T) = E_g(0 \text{ K}) + \alpha T^2 / (T + \beta), \quad (1)$$

where E_g is the band gap energy, $E_g(0 \text{ K})$ is the band gap energy at 0 K, T is the actual temperature, and α and β are fitting parameters characteristic of a given material. Table I summarizes the fitting parameters used. For comparison, in Fig. 6(b), the PL peak shift was fitted employing the expression of O'Donnell and Chen¹⁴

$$E_g(T) = E_g(0 \text{ K}) - S[E_{LO}](\coth\{E_{LO}/2kT\} - 1), \quad (2)$$

where S is a dimensionless coupling constant, k is the Boltzmann constant, and E_{LO} is the LO phonon energy ($=26 \text{ meV}$).⁴ The fitting parameters are shown in Table II. We note that the fits in Fig. 6 indicate that the scatter of the PL peak energy vanishes at higher temperatures since thermal broadening and fluctuations dominate above possible inhomogeneous sample properties accumulated from different spots.

TABLE II. Fitting parameters used with the O'Donnell–Chen relation.

Detector	$E_g(0 \text{ K})$ (eV)	S
InSb	0.8608	1.3399
InGaAs	0.8539	1.4113

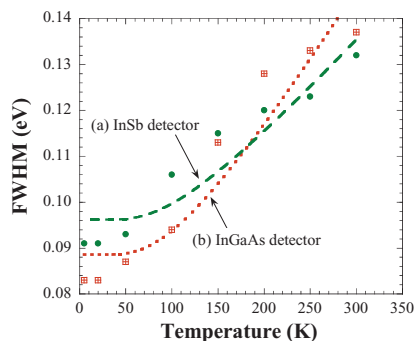


FIG. 7. (Color online) FWHM vs temperature established with (a) the InSb detector and (b) the InGaAs detector. The broken and dotted lines are fitted with Eq. (3).

It is worthwhile to stress that Eqs. (1) and (2) result in fits with a “goodness of fit value” exceeding 0.99 indicating an almost perfect agreement between theory and experiment. On the other hand, Kigel *et al.*¹⁵ reported for colloidal QDs that the Varshni relation does not predict the thermal PL peak shift for temperatures above 200 K. Apparently, the temperature dependent emission properties of PbS QDs do not possess a general and easily predictable mechanism, depending more on preparation methods and carrier materials than on intrinsic properties such as the QD diameter.

Figure 7 reveals the FWHM versus temperature of the PL peaks measured with the InSb and InGaAs detector. The behavior varies from the reported one found with PbS QDs on glass.⁴ While the PL peak shift in Fig. 6, from 5 to 300 K, is clearly larger in the current work (90 meV, rather than 55 meV in Ref. 4), the temperature induced broadening of the FWHM remains smaller (35 meV) or comparable (54 meV), for the InSb and InGaAs detector, respectively, in comparison to published values in the range of 50–60 meV. The temperature dependence of the FWHM was fitted with the Bose distribution of function of the LO phonons⁴

$$W = W(0 \text{ K}) + \gamma [\exp(E_{LO}/kT) - 1], \quad (3)$$

where $W(0 \text{ K})$ is the FWHM at 0 K and γ is a fitting constant. The fitting parameters summarized in Table III are in reasonable agreement with the previously published values in Ref. 4.

Figure 8 shows the PL intensity decrease with temperature increase in the sample. In contrast to the QDs on glass the intensity decrease reveals an overall linear decrease without the previously reported increase around 20–80 K.⁴ The linear decay without a maximum at a specific temperature is attributed to a rather constant size of the luminescent QDs.⁵ The straight lines in Fig. 8 represent a linear fit with close

TABLE III. Fitting parameters used with the Bose phonon distribution function.

Detector	W_0 (eV)	γ (eV)
InSb	0.0962	0.0680
InGaAs	0.0886	0.0999

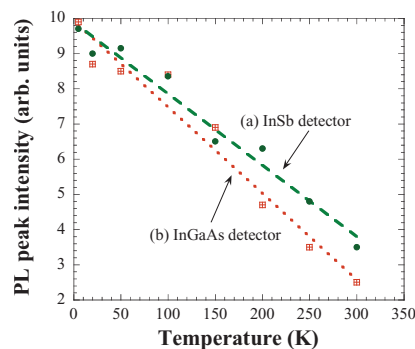


FIG. 8. (Color online) PL peak intensity vs temperature measured with (a) the InSb detector and (b) InGaAs detector. The broken and dotted lines are linear fits of the data points.

slope factors of -0.0203 and -0.0245 for the measurement carried out with (a) the InSb detector and (b) the InGaAs detector, respectively. We note that the room temperature PL peak intensity of about 25% (Fig. 2) and 35% (Fig. 3) with respect to the 5 K PL intensity clearly exceeds the 10% and 17% room temperature emission of PbS QDs on glass and colloidal QDs, respectively.^{4,15}

V. SUMMARY

In summary, the thermal dependence of the PL features of PbS QDs deposited on SI GaAs was investigated by FTIR spectroscopy. The study revealed that the deposition of PbS QDs alters the PL properties of the GaAs substrate because of charge transfer. Furthermore, we demonstrated that the temperature induced band gap shift can be fitted very well with the Varshni equation and a relation based on thermodynamic principles using the LO phonon energy of 26 meV. The latter was used as well in the Bose phonon distribution function in order to fit the FWHM of the PL peaks. The results stress that PbS/GaAs heteropairings could impact optical and optoelectronic applications in two ways: first, the QD emission intensity is relatively strong at ambient conditions (up to 35% of the cryogenic maximum) and, second, for PL enhancement of GaAs based devices operating in the near infrared spectral range. In addition, the ability to easily transfer electrons (or holes) from the dispersed QDs to GaAs layers is an important building block for heterogeneous devices.

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